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LOW-RESIN-CONTENT AND RESIN-FREE PULP PLASTICS

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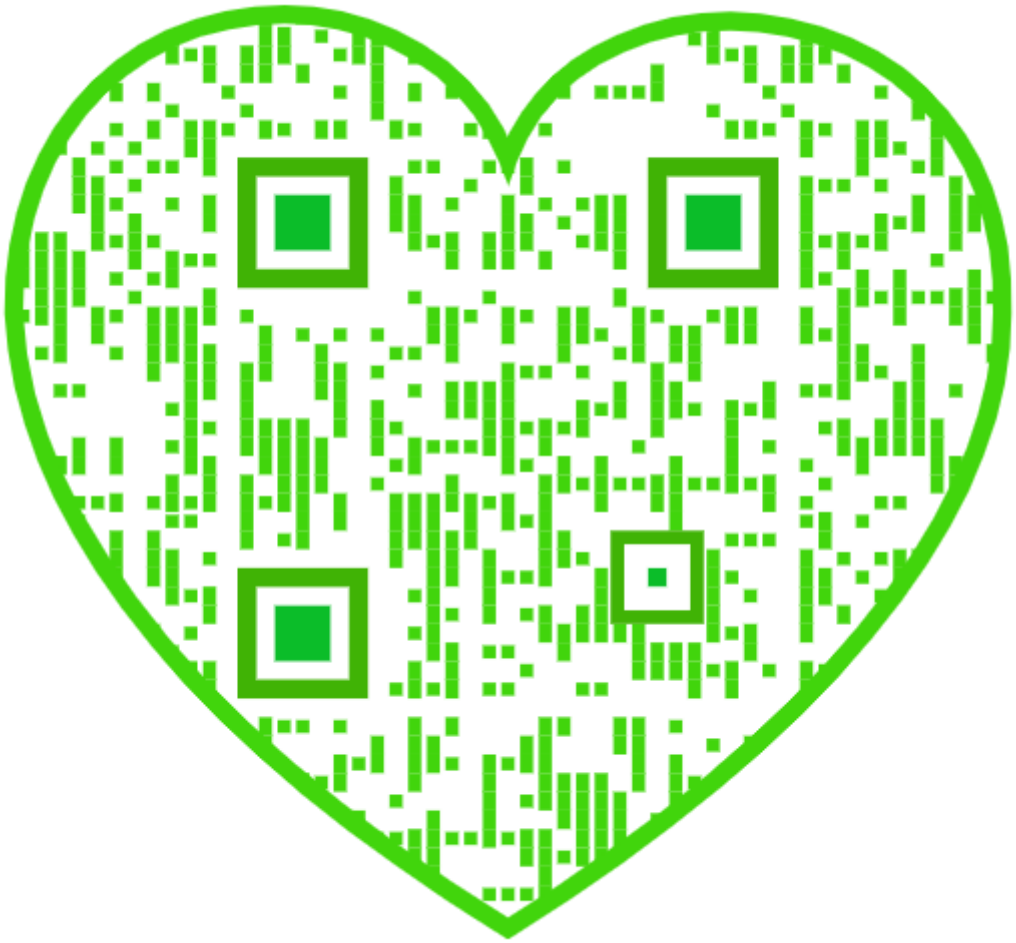

LOW-RESIN-CONTENT AND RESIN-FREE PULP PLASTICS

By

S. L. SCHWARTZ, Engineer
J. C. PEW, Engineer
and H. R. MEYER, Engineer

SUMMARY

Experiments at the Forest Products Laboratory have demonstrated that molded plastics can be made from high-yield wood pulps in which little or no phenolic resin has been incorporated. A comparison of plastics so made with pulp plastics containing as much as 40 percent of phenolic resin by weight indicated some loss of ultimate tensile and compressive strength and lowered resistance to water absorption, but improved toughness. The most promising of the plastics containing no resin appeared to be those produced from pulps obtained by milling water-cooked chips. By coating the surfaces of the pulp mats with resin before molding them, their water resistance was considerably improved. Plastics of moderate strength and good water resistance were also produced by the addition of small amounts of water-soluble phenolic resin or nonphenolic resins.

INTRODUCTION

In previous work on pulp-reinforced phenolic plastics,[1] it was found that the resin content of groundwood plastics could be greatly reduced and yet produce a pulp plastic comparable, except for water resistance, to a pulp plastic containing 40 percent of resin. The study of low-resin-content mixtures was therefore extended to include a variety of high-yield pulps.

MATERIALS

A variety of aspen and spruce pulps and a neutral sulfite semichemical pulp from a mixture of black tupelo and sweetgum were used in these experiments. The aspen group consisted of a neutral sulfite semichemical pulp, a chlorinated and extracted modification of the same pulp, a groundwood pulp, and a water-cook pulp. The spruce group consisted of an acid sulfite semichemical pulp, a water-cook pulp and a groundwood pulp.

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[1] "Pulp Reinforced Plastics", Forest Products Laboratory Mimeograph No. R1461

The chlorinated and extracted pulp was obtained by treating aspen neutral sulfite semichemical pulp with 16 percent chlorine and a 7 percent caustic soda solution. This pulp was included as an example of a completely delignified, yet relatively high-yield product. The groundwood pulps were made in the Forest Products Laboratory experimental grinder and the others by milling the treated wood chips in a double-rotating disk mill. All pulps were evaluated and used as prepared. No further processing was used or required.

Two powdered phenolic resins, one of high and one of medium fluidity, were used. The high-fluidity type worked well in the plastics with a low resin content, but was found not to be generally applicable for plastics with a high resin content. The resin of medium fluidity was therefore used in the plastics with a high resin content which are included in this study for comparison purposes. Water-soluble phenolic resins, a resinous byproduct from a wood rosin refining operation, and a soda spent-liquor lignin were used in some plastics. The powdered and water-soluble phenolic resins used for some of the plastics and the resinous byproduct from the wood rosin refining operation used in others are commercially available materials. The lignin used was an experimental material recovered from the spent liquor produced in the soda process for making paper pulp.

EQUIPMENT AND PROCEDURE

Except as otherwise noted, the plastics tested were made by suspending the pulp, powdered phenolic resin, and zinc stearate (1 percent of the mixture) in water at about 1 percent consistency. A wetting agent was used to aid in dispersing the powdered material. The stuff was formed into a mat 8-1/2 inches in diameter in a pressure-forming apparatus. The resin content was calculated on the basis of the oven-dry weight of resin retained in the mixture. The wet mat was dried in a forced circulation oven at 35° to 40° C. (95° to 104° F.) for 24 hours and conditioned at 24° C. (75° F.) and 50 percent relative humidity for at least 24 hours before being molded. The materials with a high resin content were molded between cauls for 13 minutes at 160° C. (320° F.) and drawn hot. The products containing little or no resin were also molded between cauls for 13 minutes, but the molding temperature was increased to 180° C. (356° F.), pressures of 4,000 pounds per square inch were used, and the panels were chilled before the pressure was released to prevent blistering. Although the higher molding temperature favored the moldability and improved the water resistance of the product, it is probable that lower pressures might have been adequate with some compositions. The method used to make these plastics is described in greater detail elsewhere[1].

Testing of Plastics

Strength properties were determined on specimens taken from one to four nominal 1/8-inch-thick panels of each pulp plastic. In general, the number and type of specimens taken from each panel were as follows: two tensile

specimens, two compression specimens to determine the elastic properties, four compression specimens to determine ultimate strength, five toughness specimens, and two water-absorption specimens. Tests other than toughness were made according to the methods outlined in "Federal Specifications for Plastics, Organic: General Specification (Methods of Tests) L-P-406, December 9, 1942." The toughness tests were made on the Forest Products Laboratory intermediate capacity toughness testing machine.

RESULTS

The properties of the pulps and the corresponding plastics are given in tables 1 and 2. A comparison between the phenolic plastics containing about 40 percent of resin and the corresponding resin-free pulp plastics shows that the latter products had decidedly lower ultimate tensile and compressive strengths and, usually, considerably lower proportional-limit stress values in tension. On the other hand, the toughness values increased. The plastic flow of the resin-free materials, as measured, was practically nil, and the resultant plastics had relatively poor water resistance.

By the addition of 10 to 15 percent of resin, plastics intermediate in ultimate strength, toughness, and water resistance were obtained. Compressive-yield stress and proportional-limit stress values obtained were, on the other hand, almost invariably higher for the plastics containing little resin than with those of high resin contents. In a few cases the proportional limit stress in tension was also higher. The high-fluidity resin used in the lower-resin products may have been a contributing factor in these effects.

Groundwood plastics Nos. 113 and 160 (table 2) are strong but lack toughness and water resistance when compared with the average properties of the respective aspen and spruce groups. Neutral sulfite semichemical plastics Nos. 152 and 153, on the other hand, have both strength and toughness but again have somewhat high water absorption. Plastics Nos. 211 and 212, in which pulps produced from water-cooked chips were used, have good water resistance and moderate strength. The neutral sulfite semichemical pulp which had been delignified by chlorination and caustic soda extraction produced a plastic (No. 157) which, though not water resistant, has very high toughness and exceptional elongation in tension before rupture.

Pulps molded without resin produced plastics (Nos. 169, 167, 229, 215, 216, 185 and 214E in table 2) which were high in toughness and relatively low in tensile and compressive strength but varied from extremely poor to fair in water resistance. With respect to water resistance, plastics Nos. 215 and 214E, prepared from milled water-cooked chips, were decidedly the best of the resin-free plastics.

The water resistance of all the resin-free pulp plastics may be greatly improved by surfacing them with small amounts of resin. Coating the pulp mats with water-soluble phenolic while wet, as in the cases of plastics Nos. 198 and 189B, or surfacing them with paper impregnated with phenolic resin before they were molded, as in the cases of plastics Nos. 213 and 214C,

was found to be effective. The latter method also improved the finish and permitted colored surfaces to be readily obtained.

Resinous materials other than powdered phenolic resin were added to certain high-yield pulps to aid in water resistance and moldability. By using as little as 14 percent of water-soluble phenolic resin, as with plastic No. 171, excellent water resistance was obtained in a neutral sulfite semichemical plastic. Sixteen percent of a resinous byproduct from wood rosin refining was used in plastic No. 225. In plastics Nos. 186, 226, and 187 approximately 15 percent of lignin was used. In general, these nonphenolic materials are less effective than equivalent percentages of phenolic resin, but have the advantage of lower cost.

In some instances, these compositions may be laminated instead of being molded from a pulp mat. Thus, a resin-filled paper was made from the neutral sulfite semichemical pulp (No. 5083 N in table 1), which contained 11 percent of powdered phenolic resin. The powdered resin used in this pulp was added in the beater before the stock was run on the paper machine. The resin-filled paper was molded at 180° C. (356° F.) and 4,000 pounds per square inch to form cross-laminated flat panels. The properties of the plastic thus obtained were:

Property	Value
Tensile strength	
Maximum	18,900 p.s.i.
Proportional-limit stress	6,900 p.s.i.
Modulus of elasticity	2,000,000 p.s.i.
Edgewise compressive strength	
Maximum	17,200 p.s.i.
Proportional-limit stress	3,300 p.s.i.
Modulus of elasticity	1,800,000 p.s.i.
Toughness (FPL)	16 inch-pounds per inch of width
Water absorption	7.3 percent

The reason why high-yield pulps, with or without small amounts of resin, can be readily molded into plastic-like substances has not been determined. For example, the chlorinated and extracted neutral sulfite semichemical aspen pulp, which is practically devoid of lignin, molded to a fairly dense, coherent product (plastic No. 167, table 2). The moldability of this pulp may possibly be due to the fact that its hemicellulose content is high in comparison with that of ordinary chemical pulps. It would not be expected that hemicellulose, or any carbohydrate, as a bonding agent would contribute in large measure to water resistance. In fact, the plastic has the high water-absorption value of 135 percent.

Plastics with a low water-absorption value were obtained when aspen groundwood pulps were employed, even though the lignin in wood is considered chemically combined with the hemicellulose and not available as a

plastic binder. If wood is pressed under the same conditions used with these pulps, however, some transformation, accompanied by considerable darkening in color, takes place, and a plastic-like product is formed[2]. It is logical to suppose a similar effect occurs when the wood is reduced to the form of a mechanical pulp. It is conceivable that a partial separation of the lignin from the hemicellulose occurs during the molding operation and that this "activated" lignin contributes to the moldability of the product. Still further improvement is obtained with pulps from water-cooked chips, since considerable lignin is liberated during cooking, and the weakening of the bond between the fibers allows better defibering than is possible with groundwood. More drastic cooking, it is believed, probably would not give an improved product because of the degradation of the cellulose that would be caused and the possible polymerization of the separated lignin to a more infusible state.

CONCLUSIONS

The experiments described, while exploratory in nature, indicate that high-yield pulps have definite possibilities as plastic bases, particularly for low-cost products. From a raw-material standpoint, at least, considerable reduction in cost over high-resin-content plastics is indicated.

Further investigations of cooking procedures, pulp processing, and molding compositions are, of course, needed to bring about desired improvements. The necessity of cooling the molds before drawing the plastic would in some cases be a disadvantage, especially with shaped articles. Also, since flow is generally limited, accurate and uniform preforms would be necessary. To mold flat panels, however, the pulp might be formed into boards on equipment similar to that used in making insulating board. Such potentially low-cost products may need little or no improvement for some commercial uses.

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[2] Seborg, R. M., Millett, M. A., and Stamm, A. J., "Heat-stabilized, Compressed Wood - (Staypak)" Mechanical Engineering 67, No. 1:25, January 1945. Also FPL Report No. 1500.

Table 1.--The physical and chemical properties of the high-yield pulps used for pulp plastics[1]

Pulp type	Cook or grinder run	Yield based on moisture-free wood	Freeness (Schopper-Riegler)	Bursting strength	Tearing strength	Tensile strength	Density	Cellulose content		Lignin content	Total pentosans content
								Total	Alpha		
	No.	Percent	Cc.	Points per pound per ream	Grams per pound per ream	P.s.i.	Grams per cc.	Percent	Percent	Percent	Percent
Aspen											
Neutral sulfite semichemical	5073-N	75	590	0.68	1.00	5240	0.65	80.0	62.0	12.0	18.3
Neutral sulfite semichemical, chlorinated and caustic-extracted	5073-N	58	---	---	---	---	---	98.0	79.0	.5	19.7
Groundwood	418	94	482	.19	.48	920	.38	67.0	51.0	20.9	17.9
Water cook	2	80	597	.28	.61	1760	.55	72.0	60.0	20.1	9.4
Black Tupelo and Sweetgum											
Neutral sulfite semichemical	5083-N	81	895	.10	.60	130	.24	70.0	55.0	19.7	17.7
Spruce											
Acid sulfite semichemical	5071-I	75	890	.22	1.13	660	.30	69.0	55.0	20.8	7.6
Water cook	1	85	498	.40	1.34	2230	.47	61.0	49.0	31.1	7.7
Groundwood	395	94	460	.25	.71	1420	.39	60.0	43.0	28.0	12.3

[1] Tests made according to Forest Products Laboratory standard testing methods for pulpwood, pulp, stuff, and paper.

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Table 2.--Certain properties of plastics made from high-yield pulps with or without resins

Plastic No.	No. of panels tested[1]	Pulp type	Cook or grinder run	Resin content based on total oven dry weight of mixture	Type of resin	Molding pressure	Plastic properties[2]												
							Plastic flow (diameter increase)[3]	Water absorption in 24 hours[4]	Specific gravity	F.P.L.[5] toughness	Tension					Edgewise compression			
											Ultimate strength	Proportional limit stress	Modulus of elasticity	Elongation[6]		Ultimate strength	Proportional limit stress	Modulus of elasticity	Yield strength at 0.2 percent offset
			No.	Percent		P.s.i.	In. per 1,000 p.s.i.	Percent		In. lb. per inch width	P.s.i.	P.s.i.	1,000 p.s.i.	Percent		P.s.i.	P.s.i.	1,000 p.s.i.	P.s.i.
Aspen																			
150	3	Neutral sulfite semichemical	5073-N:	41	Medium-fluidity powdered phenolic	1,500	0.23	1.8	1.37	15	19,100	5,300	1,500	2.3		16,400	2,000	1,300	5,900
153	2	Do.	5073-N:	11	High-fluidity powdered phenolic	4,000	.03	6.0	1.42	24	15,800	6,200	1,500	2.7		14,200	2,900	1,500	8,200
169	1	Do.	5073-N:	0		4,000	--	26.0	1.42	33	10,500	2,700	1,600	4.9		10,100	---	---	---
146	3	Neutral sulfite semichemical (chlorinated, caustic extracted)	5073-N:	39	Medium-flutdity powdered phenolic	1,000	.13	2.3	1.37	21	16,300	4,700	1,300	2.6		16,000	2,000	1,200	5,800
157	3	Neutral sulfite semichemical (chlorinated, caustic extracted)	5073-N:	13	High-fluidity powdered phenolic	4,000	.02	13.7	1.46	42	14,600	4,500	1,600	4.9		11,800	3,400	1,400	7,100
167	1	Neutral sulfite semichemical (chlorinated, caustic extracted)	5073-N:	0		4,000	--	135.0	1.41	40	8,500	2,100	1,100	---		6,000	---	---	---
144	3	Groundwood	418	40	Medium-flutdity powdered phenolic	1,000	.19	1.6	1.38	9	15,800	5,600	1,300	1.6		17,300	2,300	1,100	6,600
160	2	Do.	418	14	High-fluidity powdered phenolic	4,000	.06	4.8	1.40	11	15,800	8,100	1,500	1.5		13,100	3,600	1,500	8,200
229	2	Do.	418	0		4,000	--	17.9	1.43	11	9,100	3,400	1,500	1.4		6,200	3,800	1,400	---
187	2	Do.	418	14	Soda-process spent-liquor lignin	4,000	--	5.1	1.41	9	10,700	4,600	1,400	1.5		10,900	3,200	1,300	7,500
198	1	Do.	418	11	Water-soluble phenolic[7]	4,000	--	2.1	1.40	14	---	---	---	--		11,000	---	---	---
210	3	Water cook	2	39	Medium-fluidity powdered phenolic	2,000	.41	1.2	1.36	12	17,200	4,200	1,500	1.8		17,300	2,400	1,300	6,400
212	3	Do.	2	12	High-fluidity powdered phenolic	4,000	.09	2.8	1.41	14	13,600	3,900	1,700	1.5		13,300	3,100	1,600	8,400
215	2	Do.	2	0		4,000	--	6.3	1.42	18	9,200	3,600	1,500	--		9,800	3,600	1,400	7,700
225	4	Do.	2	16	Wood rosin refining byproduct	2,000	.09	3.7	1.40	12	8,300	3,200	1,400	1.6		11,000	3,800	1,300	8,200
226	1	Do.	2	15	Soda-process spent-liquor lignin	4,000	.06	3.8	1.40	12	8,000	3,700	1,300	--		9,900	---	1,300	7,500
Black Tupelo and Sweetgum																			
149	3	Neutral sulfite semichemical	5063-N:	40	Medium-fluidity powdered phenolic	1,500	.24	1.9	1.36	12	17,500	6,200	1,400	1.8		18,600	1,600	1,300	5,600
152	3	Do.	5063-N:	14	High-fluidtty powdered phenolic	4,000	.05	5.4	1.42	18	14,700	7,800	1,500	2.1		14,800	3,900	1,500	8,800
216	2	Do.	5063-N:	0		4,000	--	37.9	1.42	27	10,300	3,000	1,500	--		10,200	---	---	---
171	2	Do.	5063-N:	14	Water-soluble phenolic[8]	4,000	.05	1.9	1.41	9	12,600	7,100	2,000	.8		17,000	6,400	1,800	---
189A	1	Do.	5063-N:	2	Water-soluble phenolic[8]	4,000	--	9.6	1.44	18	10,600	2,800	2,000	2.1		10,400	3,500	1,500	---
189B	1	Do.	5063-N:	10	Water-soluble phenolic[7]	4,000	--	3.0	1.43	10	11,400	5,600	1,600	1.0		16,200	---	---	---
213	1	Do.	5063-N:	6	Spirit-soluble phenolic[9]	4,000	--	4.1	--	24	11,700	2,900	1,600	1.8		11,400	---	---	---
187	2	Do.	5063-N:	14	Soda-process spent-liquor lignin	4,000	.05	9.0	1.43	13	10,300	2,900	1,600	1.7		11,700	2,700	1,500	7,500
Spruce																			
185	3	Acid sulfite semichemical	5071-I:	41	Medium-fluidity powdered phenolic	1,000	.31	2.0	1.35	10	17,400	6,100	1,500	1.5		17,500	2,200	1,300	6,100
156	3	Do.	5071-I:	15	High-fluidity powdered phenolic	4,000	.05	6.3	1.41	13	12,100	4,800	1,500	1.7		9,600	3,100	1,500	7,800
185	1	Do.	5071-I:	0		4,000	--	24.0	1.42	15	6,900	2,900	900	2.3		4,300	---	---	---
209	1	Water cook	1	39	Medium-fluidity powdered phenolic	2,000	.25	1.2	1.36	10	18,500	6,000	1,400	1.3		18,100	3,000	1,300	7,600
211	3	Do.	1	13	High-fluidtty powdered phenolic	4,000	.08	2.7	1.38	13	11,500	3,400	1,600	1.3		12,800	2,200	1,400	7,100
214B	2	Do.	1	0		4,000	--	6.8	1.39	20	7,400	2,300	1,200	--		8,400	---	---	---
214C	1	Do.	1	5	Sprit-soluble phenolic[9]	4,000	--	2.6	1.41	--	---	---	---	--		---	---	---	---
86	4	Groundwood	395	40	Medtum-fluidity powdered phenolic	1,300	.25	1.5	1.35	7	15,500	5,800	1,400	1.4		17,100	2,700	1,300	7,500
113	1	Do.	395	12	Htgh-fluidity powdered phenolic	4,000	--	4.6	1.39	7	14,000	6,500	1,800	1.0		15,200	4,100	1,500	9,400
Commercial Phenolic Plastics[10]																			
Wood-flour filled				50		---	--	.6	1.34	2	7,100	5,500	1,000	--		23,100	3,300	1,000	---
Sisal filled				40		---	--	3.4	1.33	20	10,400	---	1,100	--		12,600	---	1,100	---
Chopped-tire cord filled				50		---	--	1.6	1.34	15	4,600	2,700	1,100	--		22,000	2,600	900	---
Aircraft-grade paper plastic (cross-laminated)				35		---	--	2.4	1.40	19	27,200	9,800	2,700	--		20,600	5,400	2,300	---

[1] Each panel furnished 2 tensile specimens, 4 compression specimens for ultimate strength determination, 2 compression specimens to determine elastic properties, 5 toughness specimens, and 2 water-absorption specimens.

[2] Properties were determined from specimens prepared, conditioned, and tested in accordance with Federal Specification for Plastics, L-P-406, Dec. 9, 1942, unless otherwise noted. Machined edges were not otherwise finished prior to test. Compressive stress-strain properties were obtained by testing a 1- by 4-inch specimen as a laterally supported column. Ultimate compressive strength was obtained by testing specimens 1 inch wide by 1/2 inch long in pairs, 1 inch apart and parallel. Values represent the average for the indicated number of tests.

[3] This value is based on the expansion of the pulp mat during molding and is considered to be a rough measure of the flowing ability of the mixture.

[4] Specimens 1/8 inch thick, 2 inches square.

[5] Forest Products Laboratory intermediate-capacity toughness machine, unnotched specimen, 3/8 inch wide by nominal 1/8 inch thickness by 3-1/2 inches long, tested over 2-1/2-inch span.

[6] Elongation immediately before fracture, measured over a 2-inch gage length.

[7] The liquid resin was brushed on the surface of the wet pulp mats.

[8] The resin was dissolved in the water used to make the pulp suspension.

[9] The pulp mat was faced on both sides with sheets of resin-impregnated paper and molded.

[10] Result of tests made at the Forest Products Laboratory.

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